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**Preparation of tertiary butyl alcohol by catalytic decomposition of tertiary butyl hydroperoxide.**

A method for preparing tertiary butyl alcohol wherein a feedstock comprising a solution of tertiary butyl hydroperoxide in a cosolvent mixture of tertiary butyl alcohol with isobutane is charged to a hydroperoxide decomposition reaction zone containing a catalytically effective amount of a hydroperoxide decomposition catalyst and is brought into contact with the catalyst in liquid phase with agitation under hydroperoxide decomposition reaction conditions to convert the tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol.

This invention relates to a method for the preparation of tertiary butyl alcohol (TBA) by the catalytic decomposition of tertiary butyl hydroperoxide (TBHP). More particularly, this invention relates to a method wherein a tertiary butyl hydroperoxide charge stock comprising a solution of tertiary butyl hydroperoxide dissolved in a cosolvent mixture of isobutane and tertiary butyl alcohol is brought into contact with a hydroperoxide decomposition catalyst in a reaction zone to convert the tertiary butyl hydroperoxide to peroxide decomposition products, principally tertiary butyl alcohol.

It is known to react isobutane with oxygen, either thermally or catalytically, to form a peroxidation reaction product wherein the principal peroxide that is formed is tertiary butyl hydroperoxide. It is also known to thermally or catalytically decompose the tertiary butyl hydroperoxide in a peroxide decomposition zone to form tertiary butyl alcohol. Normally, the unreacted isobutane is removed from the peroxidation reaction product so that the feedstock for the hydroperoxide decomposition zone is a debutanized peroxidation reaction product.

In the text entitled "Organic Peroxides" edited by Daniel Swern (Wiley Interscience, a Division of John Wiley & Sons, New York), in Vol. II on page 157 it is stated that the metal-ion-catalyzed decomposition of primary hydroperoxides yields mainly alcohols, aldehydes and carboxylic acids, citing as an example the decomposition of hydroxymethyl hydroperoxide with aqueous ferrous sulfate to provide formaldehyde, formic acid and water.

US-A-3,505,360 discloses a method wherein an alkenyl hydroperoxide is decomposed in the presence of a catalyst based on a compound of a Group IV-A, V-A or VI-A metal.

US-A-4,508,923 discloses the use of a catalyst system comprising ruthenium and chromium for decomposing organic hydroperoxides. The use of a cobalt borate catalyst for the decomposition of hydroperoxides is disclosed in US-A-4,547,598.

US-A-4,551,553 is directed to a process for the formation of alcohols such as tertiary butyl alcohol by the catalytic decomposition of an organic hydroperoxide such as tertiary butyl hydroperoxide using a binary catalyst composed of a mixture of a ruthenium compound with a chromium compound. It is stated that the use of the binary catalyst eliminates the need for stabilizing ligands.

Sanderson et al. disclose the use of a variety of catalysts for the decomposition of tertiary butyl hydroperoxide in a series of U. S. patents, including a catalyst composed of unsupported nickel, copper, chromia and iron (U. S. Patent No. 4,704,482), a catalyst composed of iron, copper, chromia and cobalt (U. S. Patent No. 4,705,903), a catalyst composed of a base treated hydrogenation catalyst from groups VIB or VIIB of the Periodic Table (U. S. Patent No. 4,742,179), a catalyst consisting essentially of nickel, copper, chromium and barium (U. S. Patent No. 4,873,380), a catalyst composed of a metal phthalocyanine promoted with a rhenium compound (U. S. Patent No. 4,910,349), a catalyst composed of a base promoted metal phthalocyanine compound (U. S. Patent No. 4,912,269), a catalyst composed of a soluble ruthenium compound promoted with a bidentate ligand (U. S. Patent No. 4,912,033), a catalyst composed of a metal porphine such as iron (III) or manganese (III) promoted with an alkyl thiol or an amine, a catalyst composed of an imidazole promoted metal phthalocyanine compound (U. S. Patent No. 4,912,266), (U. S. Patent No. 4,922,034), a catalyst composed of a metal phthalocyanine promoted with a thiol and a free radical inhibitor (U. S. Patent No. 4,922,035), a catalyst composed of a borate promoted metal phthalocyanine (U. S. Patent No. 4,922,036), or a catalyst composed of a soluble ruthenium compound and an iron compound such as an acetate, a borate, a bromide, a chloride, a 1,3-propanedionate, a 2-ethylhexanoate, an iodide, a nitrate, a 2,4-pentanedionate, a perchlorate or a sulfate (U. S. Patent No. 5,025,113).

As stated, when isobutane is reacted with molecular oxygen, the principal products of the reaction are tertiary butyl alcohol and tertiary butyl hydroperoxide. However, minor amounts of other contaminants are also formed. A minor amount of water will be formed, which will normally amount to 0.5 to 1 wt.% of the reactor effluent. The amount of byproduct water that is produced is a function of the severity of the reaction conditions employed and will tend to increase as the severity of the reaction conditions is increased.

As indicated, tertiary butyl hydroperoxide is useful as a raw material for the manufacture of tertiary butyl alcohol. The tertiary butyl alcohol can be formed by catalytic decomposition of the tertiary butyl hydroperoxide. In US-A-3,472,876, an oxygen-containing gas was charged to a reactor containing isobutane and an oxidation catalyst to provide a reaction mixture comprising tertiary butyl alcohol, tertiary butyl hydroperoxide, acetone, and tertiary butyl ether. The reported results in the patent indicate that there was comparatively low rate of conversion and a comparatively poor selectivity of the reaction to tertiary butyl alcohol.

In accordance with the present invention, a tertiary butyl hydroperoxide charge stock is used which comprises a solution of tertiary butyl hydroperoxide in a cosolvent mixture of isobutane with tertiary butyl alcohol.

A feedstock for the present invention is suitably one formed by the oxidation of isobutane with molecular oxygen to provide an oxidation reaction product containing a solution of tertiary butyl hydroperoxide in tertiary butyl alcohol and unreacted isobutane.

The tertiary butyl hydroperoxide charge stock will suitably comprise from 5 to 30 wt.% of tertiary butyl hy-

droperoxide and, correspondingly, 95 to 70 wt.% of cosolvent. The cosolvent will suitably comprise from 50 to 80 wt.% of isobutane and, correspondingly, from 50 to 20 wt.% of tertiary butyl alcohol. If the tertiary butyl hydroperoxide charge stock is an isobutane peroxidation reaction product that contains more than 30 wt.% of tertiary butyl hydroperoxide, tertiary butyl alcohol may be added in amount sufficient to provide for the desired concentration of tertiary butyl hydroperoxide in the cosolvent mixture of isobutane and tertiary butyl alcohol.

The tertiary butyl hydroperoxide charge stock is charged to a catalytic hydroperoxide decomposition zone wherein the tertiary butyl hydroperoxide is decomposed in the presence of a suitable peroxide decomposition catalyst such as a palladium catalyst.

The tertiary butyl alcohol will not be the only decomposition product that is formed. Minor amounts of other oxygen-containing materials such as those listed above will also be formed. The tertiary butyl alcohol that is recovered from the decomposition reaction mixture will be contaminated with the oxygenated impurities.

### The Catalyst System

The catalyst system to be used in accordance with the present invention is a hydroperoxide decomposition catalyst. Any suitable peroxide decomposition catalyst may be used, such as a nickel, copper, chromia, iron catalyst of the type disclosed in US-A-4,704,482; an iron, copper, chromia, cobalt catalyst of the type disclosed in US-A-4,705,903; a nickel, copper, chromium and barium catalyst of the type disclosed in US-A-4,873,380; a metal phthalocyanine catalyst of the type disclosed in US-A-4,910,349, or US-A-4,912,269; or US-A-4,922,035 or US-A-4,922,036; a ruthenium catalyst of the type disclosed in US-A-4,912,033, or US-A-5,025,113; a palladium catalyst, such as a catalyst comprising about 0.1 to 1 wt.% of palladium supported on alumina and diluted, if desired, with 100 wt.% to 500 wt.% of titania or zirconia.

### Catalytic Decomposition of Tertiary Butyl Hydroperoxide

The process of the present invention may be conducted batchwise in kettles or by continuously passing the reactants through a tubular reactor.

The catalytic decomposition of the tertiary butyl hydroperoxide is preferably conducted at a temperature within the range of 25° to 250°C. and, more preferably, at a temperature within the range of 40 to 150°C. The reaction is preferably conducted at a pressure sufficient to keep the products and reactants in liquid phase. Pressures, including autogenous pressure of 0.1 to 69 Mpa (0 to 10,000 psig), preferably 0.1 to 7.0 MPa (0 to 1,000 psig) may be used, if desired.

Flow rates of the charge solution to the reaction zone should be adjusted in order to provide an appropriate contact time within the reactor. In a batch process, the holding time may suitably be from 0.5 to 10 hours, and more preferably 1 to 3 hours. In a continuous process, the space velocity is suitably within the range of 0.5 to 2 volumes of tertiary butyl hydroperoxide charge stock per volume of pelleted catalyst per hour.

In accordance with a preferred embodiment of the present invention, isobutane is reacted with oxygen in an oxidation zone under oxidation reaction conditions including a temperature of 135 to 155°C., a pressure of 2.1 to 5.6 MPa (300 to 800 psig), and a holding time of 2 to 6 hours to provide an initial oxidation reaction product comprising unreacted isobutane, tertiary butyl hydroperoxide, tertiary butyl alcohol, and oxygen-containing by-products. The initial oxidation reaction product is then used as the tertiary butyl hydroperoxide charge stock of the present invention. If the concentration of tertiary butyl hydroperoxide in the tertiary butyl hydroperoxide charge stock is more than about 30 wt.% of the initial oxidation reaction product, the initial oxidation reaction product can be diluted with an amount of tertiary butyl alcohol sufficient to lower the concentration of the tertiary butyl hydroperoxide to a desired percentage, to provide, for example, a tertiary butyl hydroperoxide charge stock containing from 5 to 25 wt.% of tertiary butyl hydroperoxide.

The remainder of the tertiary butyl hydroperoxide charge stock will comprise a mixture of isobutane and tertiary butyl alcohol, such as a mixture comprising about 20 to 50 wt.% of tertiary butyl alcohol with, correspondingly, about 80 to 50 wt.% of isobutane.

The tertiary butyl hydroperoxide charge stock is then charged to a catalytic hydroperoxide decomposition zone where it is brought into contact with a suitable hydroperoxide decomposition catalyst to convert the tertiary butyl hydroperoxide to tertiary butyl alcohol with high yield and selectivity.

When the process of the present invention is practiced in a continuous manner by continuously charging the tertiary butyl hydroperoxide charge stock to a reactor containing a fixed bed of pelleted hydroperoxide decomposition catalyst, the space velocity is suitably in the range of 0.5 to 3 volumes of tertiary butyl hydroperoxide charge stock per volume of catalyst per hour. Preferably, the space velocity is within the range of 0.5 to 1 volume of tertiary butyl hydroperoxide charge stock per volume of catalyst per hour.

The reaction product from the tertiary butyl hydroperoxide decomposition step may then be fractionated

in any suitable manner, such as by distillation to recover the tertiary butyl alcohol.

EXAMPLES

5        The invention will be further illustrated by the following non-limiting examples.

Reactor

10        The reactor was a stainless steel tube (13mm x 736mm) which was electrically heated. Liquid feed was pumped into the bottom of the reactor. Pressure regulation was with a Skinner Uni-Flow® valve and a Foxboro® controller. The liquid feed was pumped with a Ruska® dual drive pump. Samples were collected at each space velocity and temperature using a 150 cc stainless steel bomb. The bomb was fitted with a pressure gage and rupture disk.

15        Isobutane peroxidation reactor effluent was obtained from a pilot plant peroxidation reactor.  
      Analysis of the reactor effluent was by Gas Chromatography. Details are given in the following tables.

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TABLE I

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CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

10

| <u>RUN</u> | <u>A</u>                | <u>1</u>  | <u>2</u> | <u>3</u> | <u>4</u> |
|------------|-------------------------|---|----------|----------|----------|
| 15         | Catalyst                | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |          |          |          |
|            | Catalyst (cc)           | 100   | 100      | 100      | 100      |
|            | Pressure (MPa)          | 2.1   | 2.1      | 2.1      | 2.1      |
| 20         | Feed Rate (cc/Hr.)      | 50  | 50       | 50       | 50       |
|            | Temperature (°C)        | 40  | 60       | 80       | 100      |
|            | Time on Stream (Hr)     | 4   | 4        | 4        | 4        |
| 25         | Space Vel. (cc/cc)      | 0.5   | 0.5      | 0.5      | 0.5      |
|            | TBHP Conversion (mol.%) | 56.3  | 82.7     | 92.9     | 99.6     |
|            | IB Conversion (mol.%)   | 13.1  | 0.0      | 13.4     | 3.5      |
| 30         | Sel. Acetone (mol.%)    | 0.2   | 2.3      | 6.9      | 6.8      |
|            | Sel. Methanol (mol.%)   | 0.0   | 0.2      | 0.7      | 0.5      |
|            | Sel. TBA (mol.%)        | 99.8  | 91.7     | 86.9     | 89.5     |
|            | Sel. DTBP (mol.%)       | 0.0   | 6.1      | 6.1      | 3.7      |
| 35         | <u>Composition</u>      |   |          |          |          |
|            | C3=                     | 0.019   | 0.020    | 0.023    | 0.029    |
|            | Isobutane               | 57.704  | 50.167   | 58.187   | 49.961   |
| 40         | MEOH/MF                 | 0.101   | 0.089    | 0.112    | 0.142    |
|            | Acetone                 | 1.128   | 1.139    | 1.346    | 1.875    |
|            | TBA                     | 21.338  | 38.448   | 34.791   | 43.904   |
| 45         | DTBP                    | 0.681   | 0.404    | 1.418    | 1.518    |
|            | TBHP                    | 18.084  | 7.894    | 3.126    | 1.291    |
|            |                         |   |          |          | 0.079    |

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If one compares Tables I-IV with Tables V-VII, it is clear that the selectivities to TBA are higher in the presence of isobutane. This is at least partially due to the conversion of a portion of the isobutane to TBA.

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TABLE II

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CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

| 10 | <u>RUN</u>              | <u>A</u>  | <u>5</u> | <u>6</u> | <u>7</u> | <u>8</u> |
|----|-------------------------|---|----------|----------|----------|----------|
|    | Catalyst                | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |          |          |          |          |
| 15 | Catalyst (cc)           |   | 100      | 100      | 100      | 100      |
|    | Pressure (MPa)          |   | 2.1      | 2.1      | 2.1      | 2.1      |
|    | Feed Rate (cc/Hr.)      |   | 50       | 50       | 50       | 50       |
| 20 | Temperature (°C)        |   | 40       | 60       | 80       | 100      |
|    | Time on Stream (Hr)     |   | 4        | 4        | 4        | 4        |
|    | Space Vel. (cc/cc)      |   | 0.5      | 0.5      | 0.5      | 0.5      |
|    | TBHP Conversion (mol.%) |   | 21.7     | 62.9     | 87.8     | 96.5     |
| 25 | IB Conversion (mol.%)   |   | 1.2      | n.d.     | 0.3      | 7.5      |
|    | Sel. Acetone (mol.%)    |   | 2.5      | 1.9      | 4.7      | 7.6      |
|    | Sel. Methanol (mol.%)   |   | 0.5      | 0.2      | 0.5      | 1.0      |
| 30 | Sel. TBA (mol.%)        |   | 88.4     | 92.1     | 90.6     | 88.1     |
|    | Sel. DTBP (mol.%)       |   | 9.1      | 6.0      | 4.7      | 4.3      |
|    | Composition             |   |          |          |          |          |
|    | Isobutane               | 57.704  | 56.992   | 59.018   | 57.534   | 53.360   |
| 35 | MEOH/MF                 | 0.101   | 0.108    | 0.110    | 0.131    | 0.163    |
|    | Acetone                 | 1.128   | 1.191    | 1.265    | 1.605    | 1.988    |
|    | TBA                     | 21.338  | 25.640   | 30.712   | 36.183   | 41.556   |
| 40 | DTBP                    | 0.681   | 0.971    | 1.237    | 1.291    | 1.285    |
|    | TBHP                    | 18.084  | 14.165   | 6.709    | 2.198    | 0.631    |

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TABLE III

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

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| <u>RUN</u>              | <u>A</u> | <u>9</u>  | <u>10</u> | <u>11</u> |
|-------------------------|----------|---|-----------|-----------|
| Catalyst                |          | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |           |           |
| Catalyst (cc)           |          | 100   | 100       | 100       |
| Pressure (MPa)          |          | 2.1   | 2.1       | 2.1       |
| Feed Rate (cc/Hr.)      |          | 100   | 100       | 100       |
| Temperature (°C)        |          | 60  | 80        | 100       |
| Time on Stream (Hr)     |          | 4   | 4         | 4         |
| Space Vel. (cc/cc)      |          | 1.0   | 1.0       | 1.0       |
| TBHP Conversion (mol.%) |          | 56.0  | 83.2      | 95.7      |
| IB Conversion (mol.%)   |          | n.d.  | 11.0      | 12.9      |
| Sel. Acetone (mol.%)    |          | 1.6   | 6.9       | 11.3      |
| Sel. Methanol (mol.%)   |          | 0.1   | 4.7       | 6.1       |
| Sel. TBA (mol.%)        |          | 93.0  | 88.0      | 85.2      |
| Sel. DTBP (mol.%)       |          | 5.4   | 5.0       | 3.5       |
| <u>Composition</u>      |          |   |           |           |
| Isobutane               | 57.704   | 60.017  | 51.337    | 50.249    |
| MEOH/MF                 | 0.101    | 0.106   | 0.351     | 0.477     |
| Acetone                 | 1.128    | 1.232   | 1.801     | 2.386     |
| TBA                     | 21.338   | 28.601  | 40.571    | 43.475    |
| DTBP                    | 0.681    | 1.121   | 1.292     | 1.172     |
| TBHP                    | 18.084   | 7.959   | 3.039     | 0.773     |

TABLE IV

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

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| <u>RUN</u>              | <u>A</u>  | <u>12</u> | <u>13</u> | <u>14</u> |
|-------------------------|---|-----------|-----------|-----------|
| Catalyst                | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |           |           |           |
| Catalyst (cc)           |   | 100       | 100       | 100       |
| Pressure (MPa)          |   | 2.1       | 2.1       | 2.1       |
| Feed Rate (cc/Hr.)      |   | 200       | 200       | 200       |
| Temperature (°C)        |   | 60        | 80        | 100       |
| Time on Stream (Hr)     |   | 4         | 4         | 4         |
| Space Vel. (cc/cc)      |   | 2.0       | 2.0       | 2.0       |
| TBHP Conversion (mol.%) |   | 22.6      | 67.9      | 92.4      |
| IB Conversion (mol.%)   |   | 6.1       | 16.7      | 16.9      |
| Sel. Acetone (mol.%)    |   | 5.2       | 9.1       | 15.7      |
| Sel. Methanol (mol.%)   |   | 1.3       | 1.4       | 2.9       |
| Sel. TBA (mol.%)        |   | 84.1      | 83.2      | 79.5      |
| Sel. DTBP (mol.%)       |   | 10.7      | 7.7       | 4.8       |
| <u>Composition</u>      |   |           |           |           |
| Isobutane               | 57.704  | 54.157    | 48.039    | 47.959    |
| MEOH/MF                 | 0.101   | 0.120     | 0.163     | 0.273     |
| Acetone                 | 1.128   | 1.264     | 1.849     | 2.821     |
| TBA                     | 21.338  | 28.374    | 41.215    | 44.881    |
| DTBP                    | 0.681   | 1.036     | 1.443     | 1.327     |
| TBHP                    | 18.084  | 13.996    | 5.799     | 1.383     |



TABLE V

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CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

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| <u>RUN</u> | <u>B</u>  | <u>15</u>                      | <u>16</u>                      | <u>17</u>                      | <u>18</u>                      |                                |
|------------|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 15         | Catalyst  |                                |                                |                                |                                |                                |
|            | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |                                |                                |                                |                                |                                |
|            | Catalyst (cc)                                     | 50                             | 50                             | 50                             | 50                             |                                |
|            | Pressure (MPa)                                    | 3.5                            | 3.5                            | 3.5                            | 3.5                            |                                |
| 20         | Feed Rate (cc/Hr.)                                | 25                             | 25                             | 25                             | 25                             |                                |
|            | Temperature (°C)                                  | 80                             | 100                            | 120                            | 140                            |                                |
|            | Time on Stream (Hr)                               | 4                              | 4                              | 4                              | 4                              |                                |
| 25         | Space Vel. (cc/cc)                                | 0.5                            | 0.5                            | 0.5                            | 0.5                            |                                |
|            | TBHP Conversion (mol.%)                           | 88.9                           | 93.2                           | 96.2                           | 97.4                           |                                |
|            | Selectivity IC4= (mol.%)                          | 0.0                            | -0.0                           | 0.0                            | 0.1                            |                                |
|            | Sel. Acetone (mol.%)                              | 9.7                            | 11.6                           | 13.9                           | 14.0                           |                                |
| 30         | Sel. Methanol (mol.%)                             | 1.9                            | 2.6                            | 3.3                            | 2.9                            |                                |
|            | Sel. TBA (mol.%)                                  | 82.8                           | 83.3                           | 81.6                           | 82.0                           |                                |
|            | Sel. DTBP (mol.%)                                 | 7.5                            | 5.1                            | 4.4                            | 4.0                            |                                |
| 35         | Remarks   | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis |
| 40         | <u>Composition</u>                                |                                |                                |                                |                                |                                |
|            | IC4=  | 0.001                          | 0.001                          | 0.000                          | 0.002                          | 0.007                          |
|            | MEOH/MF   | 0.016                          | 0.128                          | 0.183                          | 0.229                          | 0.208                          |
|            | Acetone   | 0.008                          | 1.072                          | 1.347                          | 1.662                          | 1.692                          |
| 45         | TBA   | 79.968                         | 94.807                         | 95.467                         | 95.799                         | 96.080                         |
|            | DTBP  | 0.055                          | 1.085                          | 0.787                          | 0.718                          | 0.663                          |
|            | TBHP  | 19.146                         | 2.126                          | 1.293                          | 0.731                          | 0.506                          |

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TABLE VI

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CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

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| RUN | <u>B</u>                 | <u>19</u>   | <u>20</u>                      | <u>21</u>                      | <u>22</u>                      |                                |
|-----|--------------------------|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 15  | Catalyst                 | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |                                |                                |                                |                                |
|     | Catalyst (cc)            | 50  | 50                             | 50                             | 50                             |                                |
|     | Pressure (MPa)           | 3.5   | 3.5                            | 3.5                            | 3.5                            |                                |
| 20  | Feed Rate (cc/Hr.)       | 50  | 50                             | 50                             | 50                             |                                |
|     | Temperature (°C)         | 80  | 100                            | 120                            | 140                            |                                |
|     | Time on Stream (Hr)      | 4   | 4                              | 4                              | 4                              |                                |
| 25  | Space Vel. (cc/cc)       | 1.0   | 1.0                            | 1.0                            | 1.0                            |                                |
|     | TBHP Conversion (mol.%)  | 78.0  | 88.7                           | 93.6                           | 97.0                           |                                |
|     | Selectivity IC4= (mol.%) | -0.0  | 0.0                            | 0.0                            | 0.1                            |                                |
|     | Sel. Acetone (mol.%)     | 9.6   | 14.9                           | 18.4                           | 20.4                           |                                |
| 30  | Sel. Methanol (mol.%)    | 1.6   | 3.2                            | 4.7                            | 5.9                            |                                |
|     | Sel. TBA (mol.%)         | 83.0  | 80.3                           | 78.1                           | 77.0                           |                                |
|     | Sel. DTBP (mol.%)        | 7.4   | 4.7                            | 3.5                            | 2.7                            |                                |
| 35  | Remarks                  | H <sub>2</sub> O Free<br>Basis                    | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis |
|     | <u>Composition</u>       |   |                                |                                |                                |                                |
| 40  | IC4=                     | 0.001   | 0.000                          | 0.001                          | 0.002                          | 0.010                          |
|     | MEOH/MF                  | 0.016   | 0.103                          | 0.212                          | 0.317                          | 0.404                          |
|     | Acetone                  | 0.008   | 0.933                          | 1.643                          | 2.135                          | 2.446                          |
| 45  | TBA                      | 79.968  | 92.570                         | 94.177                         | 94.745                         | 95.098                         |
|     | DTBP                     | 0.055   | 0.952                          | 0.706                          | 0.560                          | 0.457                          |
|     | TBHP                     | 19.146  | 4.213                          | 2.155                          | 1.233                          | 0.573                          |

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TABLE VII

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CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE  
TO TERT-BUTYLALCOHOL

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| RUN | <u>A</u>  | <u>23</u>                      | <u>24</u>                      | <u>25</u>                      | <u>26</u>                      |                                |
|-----|---|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 15  | Catalyst  |                                |                                |                                |                                |                                |
|     | .2% Pd, .08% Au on Al <sub>2</sub> O <sub>3</sub> |                                |                                |                                |                                |                                |
|     | Catalyst (cc)                                     | 50                             | 50                             | 50                             | 50                             |                                |
|     | Pressure (MPa)                                    | 3.5                            | 3.5                            | 3.5                            | 3.5                            |                                |
| 20  | Feed Rate (cc/Hr.)                                | 100                            | 100                            | 100                            | 100                            |                                |
|     | Temperature (°C)                                  | 80                             | 100                            | 120                            | 140                            |                                |
|     | Time on Stream (Hr)                               | 4                              | 4                              | 4                              | 4                              |                                |
| 25  | Space Vel. (cc/cc)                                | 2.0                            | 2.0                            | 2.0                            | 2.0                            |                                |
|     | TBHP Conversion (mol.%)                           | 45.0                           | 85.7                           | 94.5                           | 96.9                           |                                |
|     | Selectivity IC4= (mol.%)                          | -0.0                           | 0.0                            | 0.0                            | 0.1                            |                                |
|     | Sel. Acetone (mol.%)                              | 7.5                            | 15.7                           | 22.5                           | 24.1                           |                                |
| 30  | Sel. Methanol (mol.%)                             | 1.2                            | 3.9                            | 6.9                            | 7.9                            |                                |
|     | Sel. TBA (mol.%)                                  | 82.9                           | 79.9                           | 74.8                           | 73.7                           |                                |
|     | Sel. DTBP (mol.%)                                 | 9.6                            | 4.4                            | 2.7                            | 2.1                            |                                |
| 35  | Remarks   | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis | H <sub>2</sub> O Free<br>Basis |
|     | <u>Composition</u>                                |                                |                                |                                |                                |                                |
| 40  | IC4=  | 0.001                          | 0.000                          | 0.001                          | 0.006                          | 0.013                          |
|     | MEOH/MF   | 0.016                          | 0.053                          | 0.245                          | 0.461                          | 0.539                          |
|     | Acetone   | 0.008                          | 0.424                          | 1.663                          | 2.626                          | 2.894                          |
| 45  | TBA   | 79.968                         | 87.174                         | 93.373                         | 94.467                         | 94.655                         |
|     | DTBP  | 0.055                          | 0.726                          | 0.644                          | 0.458                          | 0.376                          |
|     | TBHP  | 19.146                         | 10.532                         | 2.743                          | 1.052                          | 0.602                          |

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**Claims**

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1. A method for the decomposition of tertiary butyl hydroperoxide to tertiary butyl alcohol, wherein a solution of a tertiary butyl hydroperoxide charge stock is brought into contact with a hydroperoxide decomposition catalyst, characterized in that said tertiary butyl hydroperoxide charge stock comprises a solution of ter-

tiary butyl hydroperoxide in a cosolvent mixture of isobutane with tertiary butyl alcohol.

2. A method as claimed in Claim 1, wherein the hydroperoxide decomposition catalyst is a palladium catalyst or palladium supported on alumina.
- 5 3. A method as claimed in Claim 2, wherein the alumina supported palladium catalyst is diluted with titania or zirconia.
- 10 4. A method as claimed in anyone of Claims 1 to 3, wherein a tertiary butyl hydroperoxide charge stock comprising an organic solvent solution of tertiary butyl hydroperoxide that contains from 5 to 30 wt.% of tertiary butyl hydroperoxide is brought into continuous contact with a catalytically effective amount of a pelleted hydroperoxide decomposition catalyst in a hydroperoxide decomposition reaction zone in liquid phase with agitation under hydroperoxide conversion conditions including a temperature within the range of 25° to 15 250°C, a space velocity of 0.5 to 2 volumes of tertiary butyl hydroperoxide charge stock per volume of catalyst per hour and a pressure of 0.1 to 7.0 MPa (0 to 1,000 psig) to convert said tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol, characterized in that said tertiary butyl hydroperoxide charge stock comprises a solution of tertiary butyl hydroperoxide in a cosolvent mixture of 50 to 80 wt.% of isobutane with, correspondingly, 50 to 20 wt.% of tertiary butyl alcohol.
- 20 5. A method as claimed in anyone of Claims 1 to 4, wherein the temperature is in the range of 40° to 150°C, the space velocity is within the range of 0.5 to 1 volumes of tertiary butyl hydroperoxide charge stock per volume of catalyst per hour and the pressure is 0.1 MPa.

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European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 8301

| DOCUMENTS CONSIDERED TO BE RELEVANT   |  |   |  |
|---|--|---|--|
| Category  | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X   | DE-A-32 48 465 (BAYER AG)<br>* page 4, line 22 - page 5, line 3 *<br>* page 7, line 7 - line 13 *<br>* page 8, line 5 - page 9, line 18 *<br>--- | 1-5   | C07C29/132<br>C07C29/50<br>C07C409/04        |
| D,X   | US-A-4 551 553 (TAYLOR ET AL.)<br>* column 7, line 1 - line 20 *<br>---  | 1,4,5   |  |
| X   | EP-A-0 336 480 (METALLGESELLSCHAFT AG.)<br>* page 2, line 31 - line 54 *<br>* example 1 *<br>* claim 1 *<br>---                                  | 1,4,5   |  |
| A   | US-A-5 025 113 (J.R. SANDERSON; J.F. KNIFTON)<br>whole document, esp. col. 5<br>-----  | 1-5   |  |
|   |  |   | TECHNICAL FIELDS SEARCHED (Int.Cl.6)         |
|   |  |   | C07C   |
| The present search report has been drawn up for all claims  |  |   |  |
| Place of search<br>MUNICH   |  | Date of completion of the search<br>15 February 1995  | Examiner<br>Goetz, G                         |
| CATEGORY OF CITED DOCUMENTS   |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>.....<br>& : member of the same patent family, corresponding document |  |
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